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Overtone absorption spectra of some aliphatic amines

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Abstract The infrared and near-infrared overtone absorption spectra of ethyl, n-butyl and isopropyl amines have been studied in pure and diluted form. Vibrational frequency and the anharmonicity constants for the C-H, and symmetric and asymmetric N-H stretching vibrations for the three molecules have been determined using local mode model. A dilution study clearly indicates the presence of intermolecular hydrogen bonding in all the three cases.

Keywords Absorption spectra, aliphatic amines, intermolecular hydrogen bonding, vibrational frequency, anharmonicity

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Recently, we have studied the vibrational absorption spectrum of aniline and its derivatives near 2500-16500 cm^{-1} region[1–3]. Several bands either due to overtones or due to combination of low frequency fundamentals of N-H and C-H stretch or other vibrations have been observed. The N-H stretch vibration clearly shows the presence of peak due to symmetric and asymmetric stretch vibrations, the intensity of the asymmetric stretch being slightly smaller than the symmetric one. Our curiosity to see the presence of N-H symmetric and asymmetric peaks in their fundamental and overtone bands and the intermolecular hydrogen bonding in other systems have led us to study these aliphatic amine molecules in the IR and NIR regions. A detailed study of these in the 400-13000 cm^{-1} region are reported here. To the best of our knowledge, the overtone bands of these molecules have not been studied so far except the old work of Wolff and Gamer [4].

The samples of ethyl, n-butyl and isopropyl amines were obtained from BDH (India). The reported purity of these compounds were 99% and they were used as such for experiment without any further purification. The NIR spectra were recorded using Lambda-19 UV-Vis NIR double beam spectrophotometer while for fundamental band, a JASCO FTIR-5300 spectrophotometer was used. The spectra were also recorded by putting the sample with carbon tetrachloride as solvent. For each sample, the cuvette was cleaned and rinsed properly to avoid the impurity of other compound. Several scans were made for each sample to avoid shift of peak positions and any other uncertainity. All measurements were made at room temperature (30^0C)with samples path length 1 cm.

The absorption spectra of these compounds were recorded in between 400-13000 cm^{-1} region. A part of the absorption spectrum of n-butyl amine is shown in Figure 1. The spectrum of other compounds are similar to it. The spectrum shows several peaks in 2800-3000 cm^{-1} region in all cases due to the presence of non-equivalent C-H Morse oscillators which give slightly shifted peaks in all the three compounds. There are two peaks 60-80 cm^{-1} separated from each other in the 3300-3400 cm^{-1} region. These peaks are assumed to be due to the asymmetric and the symmetric N-H stretch vibrations. The intensity of the two peaks are nearly the same in contrast to the case of aromatic compounds (aniline and its halo and alkyl derivatives) where the intensity of the two peaks are very different from each other. There also appears some weak bands in this region and they are perhaps due to the combinations. The 5800-6800 cm^{-1} is the region where first overtone due to CH and NH bands are expected and in the spectrum of all the three molecules, this region appears very much crowded. Though both the peaks for the N-H vibration (but the asymmetric stretch peak now appears weak than the symmetric stretch) appear in this region, the number of

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peaks for CH stretch vibrations are reduced. Some very weak bands appear here again due to the combination of first overtone of CH and NH stretch or with other fundamentals or with their

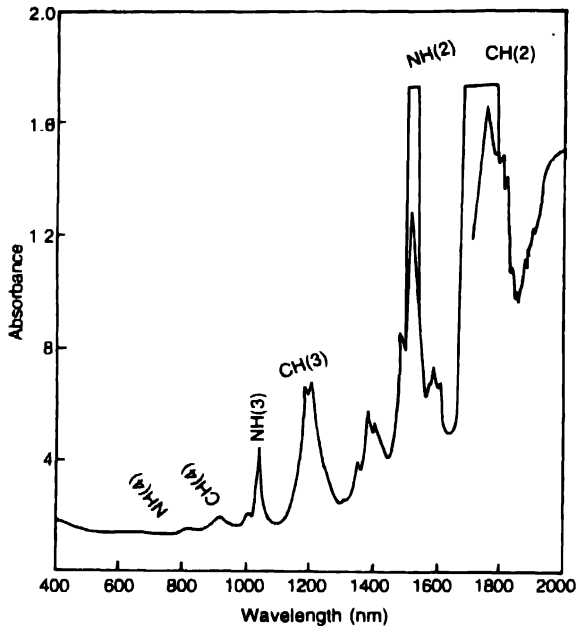

Figure 1. The vibrational absorption spectrum of n-butylamine

deformations. The number of peaks are further reduced as we go to the higher harmonics so that only one peak appears for the 3←0 and 4←0 transitions for the C-H stretch vibration. The asymmetric peak of the N-H vibration becomes too weak to be detected for 4←0 transition. Although some combination bands appear in this region, their intensity is very small. The band width of the peak increases every time as we go to the higher harmonics. The frequency of the bands and their vibrational assignments for the three molecules are given in Table 1. The spectrum of n-butylamine and the assignments of the bands observed is shown in Figure 1.

Table 1. Transition frequencies (cm^{-1}) for ethyl,n-butyl and isopropyl amines

Sample	1←0	2←0	3←0	4←0
Ethyl amine (C-H)	2950.1	5772.8	8430 5	11022 2
(N-H sym)	3338.2	6536.7	9581.8	12407.2
(N-H asym.)	3393.4	6684.3	9840.1	
N-butyl amine (C-H)	2928.2	5698.7	8411 0	10934.3
(N-H sym.)	3323.6	6544.3	9575.9	12440.1
(N-H asym.)	3379.6	6691 4	9827 3	
Isopropyl amine(C-H)	2955.3	5769 3	8431.3	11025.6
(N-H sym.)	3317.8	6503 8	9557.1	12397 1
(N-H asym.)	3387.1	6712.0	9860.1	

As mentioned earlier for fundamental and first overtone transitions, two to three peaks are observed for C-H stretch vibration in all the three molecules. However, only one peak appears for second and third overtones as if the energy corresponding to all the non-equivalent C-H oscillators are concentrated in only one band. A Morse plot in between E/ν

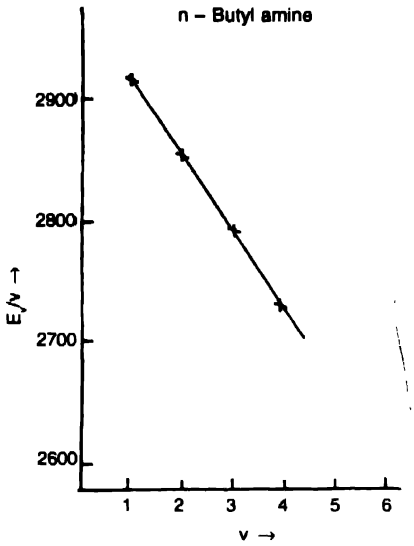

Figure 2. A Morse plot E_v/v *versus* v for n-butylamine

versus v for n-butylamine molecule is shown in Figure 2 The transition frequency for different vibrations for all the three molecules were fitted by least square fit method using local mode model

$$\Delta E_v = Av + Bv^2,$$

where E_v is the transition frequency, v is the vibrational quantum number and A and B are the fitting constants related with actual molecular constants as $w_e x_e = -B$ and $w_e = A - B$. The w_e and $w_e x_e$ values and the errors estimated for all the three vibrations in the three molecules, are given in Table 2. The low frequency fundamentals and the combination bands and their assignments are given in Table 3 (a), (b) and (c). A comparison of these values in the three molecules indicate that they are nearly same The combination bands may be either due to local mode-local mode combination or due to normal mode-local mode combination or due to normal mode-normal mode combinations In our case, we observe only normal-normal and normal-local

Table 2. Vibrational frequencies, anharmonicity constants and dissociation energies for the C-H stretch vibrations in ethyl,n-butyl and isopropyl amines.

Sample	A (cm^{-1})	$-B = w_e x_e$ (cm^{-1})	$w_e = A - B$ (cm^{-1})	$D_e = w_e^2/4 w_e x_e$ (eV)
Ethyl amine	3004.7 ±4.6	62.5 ±2.3	3067.5 ±6.9	4.6 ±0 15
N-butyl amine	2995.1 ±11.1	65.3 ±3.2	3060.4 ±14.3	4 4 ± 16
Isopropyl amine	3001.3 ±7.4	61.6 ±2.1	3062.9 ±9.5	4 7 ± 13

For N-H stretch vibration

Sample	A (cm^{-1})	-B= $w_e x_e$ (cm^{-1})	w_e=A-B (cm^{-1})	D_e= $w_e^2/4\ w_e x_e$ (eV)
Ethyl amine	3413 5 ±1.6	73.09 ±0.6	3486 5 ±2 2	5.15 ±0.0
	3457.5 ±6.3	58 9 ±2.4	3516.5 ±8 7	6 49 ±0 2
N-butyl amine	3418.1 ±8 9	76 5 ±2.6	3494.6 ±11.5	4.95 ±0.1
	3456.2 ±12 6	59 5 ±4.7	3515 7 ±17 3	6 4 ±0.4
Isopropyl Amine	3416.2 ±7 4	78.8 ±2.1	3495 0 ±9.5	5 08 ±0 4
	3463.4 ±13.3	58 2 ±5 0	3521 7 ±18.4	6 6 ±0.5

Table 3 (a). Combination bands in ethyl amine, n-butyl amine and isopropyl amine and their assignments.

Frequency(cm^{-1})	Assignments
890 0	C-C stretch
1092 1115, 1280	δ_{CH} (bend)
1460 0	δ_{CH} (bend)
1493 0	δ_{CH} (bend)
1620 0	NH deformation
2880 0	Overtone of the asymmetric CH_3 deformation
2965 0	Combination band
5486 3	$\upsilon_{CH}+2\delta_{CH}$
6414 1	$\upsilon_{NH}^{1-0}+\upsilon_{CH}^{1-0}$
7156 4	$2\upsilon_{CH}+\delta_{CH}$
7335 2	$2\upsilon_{CH}+\delta_{CH}$
8107 5	$2(\upsilon_{CH}+\delta_{CH})$

Table 3 (b).

Frequency(cm^{-1})	Assignments
890 0	C-C stretch
1097,1120, 1274	δ_{CH} (bend)
1462 0	δ_{CH} (bend)
1494 0	δ_{CH} (bend)
1625 0	NH deformation
2885 0	Overtone of the asymmetric CH_3 deformation
2970 0	Combination band
5434 2	$\upsilon_{CH}+2\delta_{CH}$
6280 6	$\upsilon_{NH}^{1-0}+\upsilon_{CH}^{1-0}$
7270 5	$2\upsilon_{CH}+\delta_{CH}$
7307 4	$2\upsilon_{CH}+\delta_{CH}$
8248 3	$2(\upsilon_{CH}+\delta_{CH})$

Table 3 (c).

Frequency (cm^{-1})	Assignments
802 0	C-C stretching
809.0	C-C stretch
1086, 1131, 1245	δ_{CH} (bend)
1447	δ_{CH} (bend)
1462 0	δ_{CH} (bend)
1608 0	NH deformation
2870 0	Overtone of the asymmetric CH_3 deformation
2965 0	Combination band
5413 4	$\upsilon_{CH}+2\delta_{CH}$
6285 0	$\upsilon_{NH}^{1-0}+\upsilon_{CH}^{1-0}$
7124.3	$2\upsilon_{CH}+\delta_{CH}$
7342 3	$2\upsilon_{CH}+\delta_{CH}$
8130.4	$2(\upsilon_{CH}+\delta_{CH})$

combinations. The frequency of combination bands in the case of normal-local combination is given as

$$\Delta E(v_1, v_2;0) = v_1(A_1 + v_1 B_1) + v_2(A_2 + v_2 B_2) + v_1 v_2 X_e ,$$

where A_1, B_1 and A_2, B_2 are the mechanical constants for the two vibrations and X_e is the coupling coefficient.

The calculated values of the off-diagonal local-normal interaction constant for $(\upsilon_{CH} + \delta_{CH})$ for the three molecules are given in the Table 4.

Table 4. Off-diagonal Local-Normal coupling coefficient X_e

Groups involved in coupling	X_e
Ethyl amine $(\upsilon_{CH}+\delta_{CH})$	– 12.51
n-Butyl amine $(\upsilon_{CH}+\delta_{CH})$	– 25 53
Isopropyl amine $(\upsilon_{CH}+\delta_{CH})$	– 15 37

Overtone bands due to N-H stretch vibrations :

The N-H stretch vibration show well resolved double peak, the intensity of the one component lying in the lower energy side is smaller than the other one for the harmonics. The frequencies of the bands are given in Table 1. The vibrational frequency and the anharmonicity constants for the symmetric and the asymmetric stretch vibrations from the fit are given in Table 2. It is noted that the vibrational frequency and the anharmonicity constants for the symmetric stretch are identical for all the three cases. A similar thing is with the asymmetric vibration. The frequency of asymmetric stretch is larger than symmetric stretch. It is interesting to note that as we go from symmetric to asymmetric vibration, the vibrational frequency though changes by 1-2%, the anharmonicity constants change by >20%. It is much smaller in the case of asymmetric stretch vibration.

Table 5. Effect of dilution on the NH symmetric stretch vibration in the three aliphatic amines.

Dilution (%)	1←0	2←0	3←0
100	3338.2♣	6536 7♣	9581 8♣
	3323 6♦	6544.3♦	9575 9♦
	3317.8♠	6503 8♠	9557 1♠
50	3356 2♣	6550 7♣	9587.1♣
	3335.4♦	6556.6♦	9585 1♦
	3341 0♠	6520.0♠	9571 0♠
20	3366 1♣	6560.3♣	9591 3♣
	3345.5♦	6565 5♦	9590.4♦
	3356 4♠	6534 4♠	9580.1♠
10	3376 8♣	6564.4♣	9595.3♣
	3353.5♦	6570 0♦	9593 8♦
	3362 2♠	6544 8♠	9585 2♠
1	3384.1♣	6566 2♣	9598.1♣
	3360 7♦	6574 6♦	9596.5♦
	3365 4♠	6549 6♠	9586 4♠
0.1	3389.3♣	6568.5♣	9600.2♣
	3367.5♦	6577 1♦	9598.4♦
	3369.6♠	6551.7♠	9587.0♠

♣- N-H stretch frequencies for ethyl amine

♦- N-H stretch frequencies for n-butyl amine.

♠- N-H stretch frequencies for isopropyl amine

We also recorded the spectrum of the three molecules at different dilutions (100%,50%,20%,10%,1%,0.1%)using carbon tetrachloride as solvent. The spectrum of the n-butylamine at different dilution is shown in Figure 3. One can see from the figure that the N-H peak clearly shows a blue shift as we go to higher dilution. However, the shift is much smaller compared to the shift observed in the compounds containing OH group (see Table 5). The compounds containing OH group are strongly hydrogen bonded through the electronegative element O and forms higher oligomers. On dilution, the hydrogen bonds break and monomers are formed which give sharp peaks nearly 250 cm^{-1} shifted in the higher frequency side. In the compounds containing amino group, the hydrogen bondings are relatively weak as N is less electronegative than O. In this case also on dilution, monomers are formed very much similar to the earliar case. Our measurements show that these monomers are only 40-50 cm^{-1} shifted in the higher frequency side from the associated peak and therefore in this case, they are not well-resolved with the associated peak. The intensity of the associated peak decrease with dilution and that of the monomer increases. As a result, the monomer peak starts dominating and overall peak shifts. At higher dilution, most of the molecules are in monomer form and it shows a saturation.

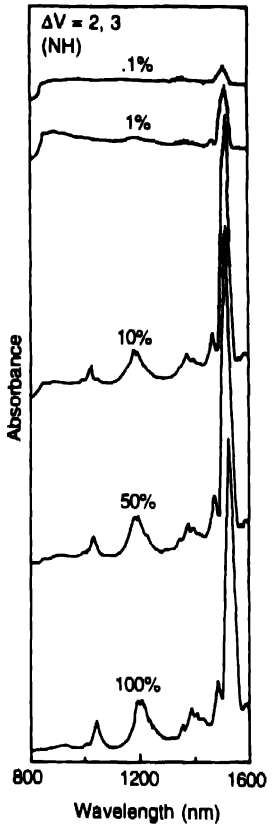

Figure 3. Effect of dilution on the absorption spectrum of n-butylamine

As we go to the cases of higher overtones the shift decrease This demonstrates the effect of chlorine atom from CCl_4 on N-H bond as the amplitude of N-H bond increases. This is again very much identical to what have been observed in the molecules containing hydroxyl radical [5]

Acknowledgments

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References

[1] J Vipin Prasad, S B Rai and S N Thakur *Indian J Phys* **69B** 315 (1995)

[2] Vineet Kumar Rai, D K Rai and S B Rai *Spectrochim Acta* **A59** 1299 (2003)

[3] Vineet Kumar Rai, A K Rai, D K Rai and S B Rai *Spectrochim Acta A* (in press)

[4] H Wolff and G Gamer *J.Phys.Chem.* **76** 871 (1972)

[5] P K Srivastav, D K Rai and S B Rai *Spectrochim Acta* **A56** 1283 (2000)